

high temperature pyrolysis (>550 °C) and is a good absorbent (Downie *et al.*, 2009). On the other hand, low temperature pyrolysis (<550 °C) favors recovery of carbon and other nutrients (i.e. N, P, K, S) as these nutrients are increasingly lost at high temperature. Due to high reactivity in soil, it has better contribution to soil fertility (Steinbeiss *et al.*, 2009; Joseph *et al.*, 2010).

Carbon sequestration potential and soil quality improvement are the main objective behind the production of biochar. For optimized biochar production, temperature ranging from 350-800 °C (on pyrolysis). By increasing pyrolysis temperature, the yield of biochar decreases and vice versa. Higher yield of biochar obtained at slow pyrolysis and has a potential role of carbon sequestration although they are less aromatic as well as less stable than biochar produced at higher. Gaseous and liquid products are produced at high pyrolysis temperature (Bridgewater and Peacocke, 2000). During high temperature pyrolysis reduces oxygen and increases carbon in biochar (Spokas, 2010).

Dark brown liquid is formed at fast pyrolysis in the absence of oxygen which is a high temperature process and this liquid is known as “Bio-Oil”. Slow pyrolysis is especially used for making biochar (Bridgewater and Peacocke, 2000). Bio-oil can be easily stored, transported and be used for production of chemicals and energy. In gasification process, during which fuel gas is produced which can be used for combustion and in engine or turbine for electricity production. So, main product is bio-oil (80%) during fast pyrolysis together with fuel gas and char (Bridgewater, 2000).

### 2.1. Physical properties of biochar

Extremely small size of biochar particle results in greater surface area and low bulk density ( $0.3 \text{ Mg m}^{-3}$  as compared to average soil bulk density of  $1.3 \text{ Mg m}^{-3}$ ). Solid and bulk are two type of densities of biochar to identify the biochar from physical point of view (Downie *et al.*, 2009).

Density on a molecular level is solid density, whereas bulk density is that of the material consisting of multiple particles. An inverse relation between bulk and solid densities exist in biochar due to pore

development during pyrolysis, and it is due to removal of –OH (hydroxyl ion) group called dehydroxylation whereby water molecules break all walls and make biochar more porous in nature (Downie *et al.*, 2009). There are a range of particle size of biochar material depending upon temperature and method of production. Fine texture biochar (<0.002 mm diameter) is produced at high temperature which is fast pyrolysis with short burning time and vice versa (Dall’Ora *et al.*, 2008). During pyrolysis, heating rate and production temperature have good effect on pore structure and surface area development. It was also found that at lower temperature formation of pores is stopped as result of tars obtained from wood decomposition during formation of biochar. These pores become easily accessible at temperature 750 °C or more (Van Zwaitan *et al.*, 2010).

### 2.2. Chemical properties of biochar

Biochar has high carbon content which comprises of aromatic rings of six carbon atom without oxygen and hydrogen (Schmidt and Noack, 2000). Due to high variability and complexity, biochar has escaped full characterization. The mineral components which is present in carbon structure of biochar differ in structural ordering, magnetic and electrical properties (Yao *et al.*, 2010).

Chan and Xu (2009) reported that during pyrolysis the time, temperature and heating rate directly affect the chemical properties of biochar. The pH and EC of biochar depends on content and composition of mineral fraction and which in turn depend upon the type of feedstock and pyrolysis condition under which it has been produced (Chan and Xu, 2009; Singh *et al.*, 2010). High reactivity of the surface of biochar particles in soils is due to presence of reactive functional groups (OH, COOH) some of which are pH dependent (Cheng and Lehmann, 2009). Higher tendency is the major characteristic of biochar which is higher than organic matter to attract cations per unit of carbon. This higher tendency is due to large surface area and more negative charge per unit area (Liang *et al.*, 2006).

The polycyclic aromatic hydrocarbons (PAHs) are significantly present in wood but depend upon temperature. Retene (a high molecular weight PAH)

was present at a rate of 3600 ng g<sup>-1</sup> biochar at 450 °C whereas in natural char, the value was much higher (21000 ng g<sup>-1</sup> biochar at 500 °C). It was also observed that low molecular weight and high vapor pressure PAHs was present at low temperature biochar and vice versa. Another chemical property of biochar is H: C ratio. It decreases with increasing carbonization temperature and this decrease means that there is increased removal of hydrogen. Structural arrangement of biochar is also related to this H: C ratio property (Brown, 2009).

The stability of biochar is dependent on O: C ratio and is also an indicator of black carbon oxidation. The O: C ratio does not only depend on temperature but also depends upon parent material and post production conditions. By increasing pyrolysis temperature, the ratio decreases. So a stable biochar is produced when O: C ratio is low. Across a range of temperature (300-1000 °C), biochar having O: C ratio < 0.2 have higher stability with half-life of greater than 1000 years (Spokas, 2010).

### 2.3. Nutrients concentration and availability in biochar

The biochar has good nutrients value either directly supplied to plant or indirectly to soil for its improvement. Direct nutrients release is measured in terms of nutrients availability whereas indirect is measured in term of its ability to be retained in soil by reducing leaching losses (Chan and Xu, 2009). The leaching losses of nutrients can be minimized by nutrient adsorbing capacity of biochar in sandy soils with low clay contents (Major *et al.*, 2009; Van Zwietaan *et al.*, 2010).

The type and rate of interaction of biochar to other nutrients in soil depend on feedstock, pyrolysis process, particle size and soil environment (Steiner *et al.*, 2007; Brunn *et al.*, 2008; Kuzyakov *et al.*, 2009). The kind of feed stocks and processing conditions are two main things on which nutrient composition of biochar is dependent, whereas availability of nutrients depends upon adsorption capacity of the biochar (De Luca *et al.*, 2009; Singh *et al.*, 2010; Yao *et al.*, 2010). Phosphorous is present in ash fraction and reactions depend on pH and presence of chelating substances that covers phosphate solubilization. Availability of N

depends upon type of biomass, heating rate and final pyrolysis temperature (Amonette and Joseph, 2009; De Luca *et al.*, 2009). The total nutrient composition and pH of biochar from different feed stocks are given in Table 1.

By increasing ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>) retention, and reducing nitrous oxide (N<sub>2</sub>O) emission and nitrate (NO<sub>3</sub><sup>-</sup>) leaching, biochar has the ability to retain nitrogen in soils (Clough and Condron, 2010). The biochar made from bamboo at pyrolysis temperature had significant effect on ammonia adsorption capacity. When biochar was pyrolyzed at 500 °C there was maximum adsorption of ammonia which is due to presence of acidic functional group. So, by increasing pyrolysis temperature there is decrease of acidic functional groups. A similar result was found by Kastner *et al.* (2009), exposing palm biochar at 500 °C to ammonia and has adsorption capacity of 0.70 mg g<sup>-1</sup> biochar (Asada *et al.*, 2006).

### 2.4. Effect of biochar application on soil properties

#### 2.4.1. Effect of biochar on physical properties of soil

The structure, bulk density and pore size which are physical properties of soil can be changed by addition of biochar which results in increased soil aeration in fine textured soil (Table 2), improved nutrient retention for plants and increased soil moisture availability (Chan *et al.*, 2007; Kolb, 2007; Downie *et al.*, 2009). The increased moisture retention depends on higher porosity of biochar. Soils amended with biochar is more effective in sandy soils than in loamy and clay soils by improved water holding capacity (Glaser *et al.*, 2002; Gaskin *et al.*, 2008).

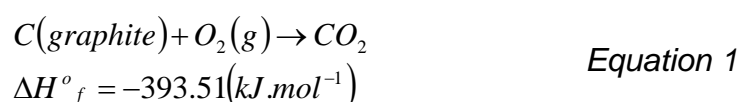
The biochar reduces soil compaction because it has lower bulk density as compared to other minerals. But the added biochar can also fill up the pore spaces thereby increasing soil density (Verheijen *et al.*, 2009). The method of biochar application with heavy machinery can compact the subsoil and as well as time, mobility and fate of biochar has impact on soil (Doerr *et al.*, 2000). Recent studies have shown that soils amended with biochar have increased mycorrhizal growth in soil along with increased growth of roots resulting in improved soil structure (Downie *et al.*, 2009; Verheijen *et al.*, 2009).

Biochar pores are classified in this review into three categories (Downie et al., 2009), according to their internal diameters (ID): macropores (ID >50 nm), mesopores (2 nm < ID < 50 nm) and micropores (ID < 2 nm). These categories are orders of magnitude different to the standard categories for pore sizes in soil science (see Table 3.1). The elementary porosity and structure of the biomass feedstock is retained in the biochar product formed (Downie et al., 2009). The vascular structure of the original plant material, for example, is likely to contribute for the occurrence of macropores in biochar, as demonstrated for activated carbon from coal and wood precursors (Wildman and Derbyshire, 1991). In contrast, micropores are mainly formed during processing of the parent material. While macropores have been identified as a 'feeder' to smaller pores (Martinez et al., 2006), micropores effectively account for the characteristically large surface area in charcoals (Brown, 2009).

opposite was found for almond shell, probably due to its inherently high initial thermal decomposition rate (González et al., 2009).

## 2.4 Thermodynamic stability

The thermodynamic equilibrium concerning carbonised residues, such as biochar, favours the production of CO<sub>2</sub>.



The standard enthalpy of formation is represented as  $\Delta H^{\circ}_f$  and the degree sign denotes the standard conditions (P = 1 bar and T = 25°C)

Equation 1 shows that the oxidation of graphite, being the most thermodynamically stable form of carbon, will occur spontaneously as shown by the negative energy value (meaning that 393.51 kJ of energy is emitted for every mole of CO<sub>2</sub> 'produced'). Since the oxidation of graphite to carbon dioxide will occur, albeit very slowly under normal conditions (Shneour, 1966), all other forms of carbon which are less thermodynamically stable than graphite, will also undergo oxidation to CO<sub>2</sub> in the presence of oxygen. The speed at which this oxidation occurs depends on a number of factors, such as the precise chemical composition, as well as the temperature and moisture regime to which the compound is exposed. Furthermore, residence time of biochar in soils will also be affected by microbial processes. The recalcitrance of biochar in soil is discussed in more depth in Sections 3.2.1 and 3.2.5.1.

## 2.5 CEC and pH

CEC variation in biochars ranges from negligible to around 40 cmol<sub>c</sub> g<sup>-1</sup> and has been reported to change following incorporation into soils (Lehmann, 2007). This may occur by a process of leaching of hydrophobic compounds from the biochar (Briggs et al., 2005) or by increasing carboxylation of C via abiotic oxidation (Cheng et al. 2006; Liang et al. 2006). Glaser et al. (2001) discussed the importance of ageing to obtain the increases in CEC of black BC found in the Terra Preta soils of the Amazon.

Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, that is to say they are largely neutral to basic. Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6. The lower end of this range seems to be from green waste and tree bark feedstocks, with the higher end from poultry litter feedstocks.

## 2.6 Summary

Biochar is comprised of stable carbon compounds created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is typically > 7. Some properties are pervasive throughout all biochars, including the high C content

and degree of aromaticity, partially explaining the high levels of biochar's inherent recalcitrance. Nevertheless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type and the pyrolysis conditions (mainly temperature) used. These same parameters are key in determining particle size and pore size (macro, meso and micropore; distribution in biochar. Biochar's physical and chemical characteristics may significantly alter key soil physical properties and processes and are, therefore, important to consider prior to its application to soil. Furthermore, these will determine the suitability of each biochar for a given application, as well as define its behaviour, transport and fate in the environment. Dissimilarities in properties between different biochar products emphasises the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site. Further research aiming to fully evaluate the extent and implications of biochar particle and pore size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate (see Section 3.2.1).